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(54) Title: PULP-MODIFIED BICOMPONENT CONTINUOUS FILAMENT NONWOVEN WEBS		
(57) Abstract Absorbent nonwoven web composites exhibit a combination of excellent strength, softness and absorbency. The composites utilize a combination of substantially continuous bicomponent thermoplastic filaments, and pulp fibers. The substantially continuous bicomponent filaments distribute liquid insults and contribute durability and softness. The pulp fibers and, optionally, a superabsorbent, absorb and contain the liquid.		

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PULP-MODIFIED BICOMPONENT CONTINUOUS FILAMENT NONWOVEN WEBS

FIELD OF THE INVENTION

This invention relates to nonwoven web composites which exhibit a combination of excellent strength, softness, flexibility and absorbency. More specifically, the invention is directed to nonwoven web composites including a combination of pulp and thermoplastic bicomponent continuous filaments. The pulp may be mixed with one or more superabsorbent materials.

BACKGROUND OF THE INVENTION

This invention is directed to a superior nonwoven web composite product having a variety of desirable properties.

Bicomponent nonwoven filaments are known in the art generally as thermoplastic filaments which employ at least two different polymers combined together in a heterogeneous fashion. Instead of being homogeneously blended, two polymers may, for instance, be combined in a side-by-side configuration, so that a first side of a filament is composed of a first polymer "A" and a second side of the filament is composed of a second polymer "B." Alternatively, the polymers may be combined in a sheath-core configuration, so that an outer sheath layer of a filament is composed of a first polymer "A," and the inner core is composed of a second polymer "B." Alternatively, the polymers may be combined in an island-in-the-sea configuration in which one or more islands of a first polymer "A" appear in a sea of a second polymer "B." Other heterogeneous configurations are also possible.

Bicomponent filaments offer a combination of desired properties. For instance, certain polypropylene resins yield filaments which are strong but not particularly soft. Certain polyethylene resins yield filaments which are soft but not particularly strong. By combining both resins together in the form of bicomponent nonwoven filaments, a hybrid combination of strength and softness can be achieved.

Bicomponent filaments have been disclosed in combination with carbon particles, zeolites, ion exchange resins, carbon fibers, sterilizing fibers, and/or gas adsorbing fibers for use in specialized filters. U.S. Patent 5,670,044, issued to Ogata et al., discloses the use of bicomponent meltblown filaments in these combinations, for use in cylindrical

filters. In that case, the bicomponent filaments contain high and low melting polymers. The filaments of the filter are stacked and bonded together by melting only the lower melting component.

Pulp fibers have been employed in certain absorbent applications, to enhance the absorbency. U.S. Patent 4,530,353, issued to Lauritzen, discloses pulp fibers in combination with staple length bicomponent fibers used in the manufacture of absorbent bandages. In that case, the fibers also contain high and low melting polymers. The staple length fibers are bonded together by melting only the lower melting component.

There is a need or desire for an absorbent nonwoven web composite which exhibits a combination of durability and softness, and good distribution of liquids. This need exists for diapers, training pants, wipes, and other personal care absorbent articles where comfort, strength, and absorbent performance are all important.

SUMMARY OF THE INVENTION

The present invention is directed to an improved absorbent nonwoven web composite, and a personal care absorbent article constructed using the improved composite. The absorbent nonwoven web composite includes a matrix web of substantially continuous length bicomponent thermoplastic nonwoven filaments. A quantity of pulp fibers is contained within the continuous filament matrix.

The substantially continuous bicomponent filaments, which are uncut in length during nonwoven web formation, provide better distribution of liquids than staple length filaments, which are chopped into relatively short lengths ranging from less than one inch to a few inches. Preferably, the polymers in the bicomponent filaments are selected so that at least one of the polymers provides strength and durability, and at least one of the polymers provides softness, to the nonwoven web. Absorbent pulp fibers, which may constitute up to about 97% by weight of the absorbent nonwoven web composite, are better contained within the matrix of continuous filaments having strength and durability, as well as long length.

With the foregoing in mind, it is a feature and advantage of the invention to provide an absorbent nonwoven web composite having a combination of durability and softness.

It is also a feature and advantage of the invention to provide an absorbent nonwoven web composite capable of containing high pulp loadings within a continuous filament matrix, whether the pulp fibers are in a wet or dry state. A superabsorbent material may also be contained within the continuous filament matrix.

It is also a feature and advantage of the invention to provide an absorbent article, for example a diaper, which exhibits comfort, strength and excellent performance due to the absorbent nonwoven web composite of the invention.

DEFINITIONS

The term "nonwoven fabric or web" means a web having a structure of individual fibers or threads which are interlaid, but not in a regular or identifiable manner as in a knitted fabric. Nonwoven fabrics or webs have been formed from many processes such as, for example, meltblowing processes, spunbonding processes, air laying processes, and bonded carded web processes. The basis weight of nonwoven fabrics is usually expressed in ounces of material per square yard (osy) or grams per square meter (gsm) and the fiber diameters useful are usually expressed in microns. (Note that to convert from osy to gsm, multiply osy by 33.91).

The term "microfibers" means small diameter fibers having an average diameter not greater than about 75 microns, for example, having an average diameter of from about 1 micron to about 50 microns, or more particularly, having an average diameter of from about 1 micron to about 30 microns. Another frequently used expression of fiber diameter is denier, which is defined as grams per 9000 meters of a fiber. For a fiber having circular cross-section, denier may be calculated as fiber diameter in microns squared, multiplied by the density in grams/cc, multiplied by 0.00707. A lower denier indicates a finer fiber and a higher denier indicates a thicker or heavier fiber. For example, the diameter of a polypropylene fiber given as 15 microns may be converted to denier by squaring, multiplying the result by .89 g/cc and multiplying by .00707. Thus, a 15 micron polypropylene fiber has a denier of about 1.42 ($15^2 \times 0.89 \times .00707 = 1.415$). Outside the United States the unit of measurement is more commonly the "tex," which is defined as the grams per kilometer of fiber. Tex may be calculated as denier/9.

The term "spunbonded fibers" refers to small diameter fibers which are formed by extruding molten thermoplastic material as filaments from a plurality of fine

capillaries of a spinnerette having a circular or other configuration, with the diameter of the extruded filaments then being rapidly reduced as by, for example, in U.S. Patent 4,340,563 to Appel et al., and U.S. Patent 3,692,618 to Dorschner et al., U.S. Patent 3,802,817 to Matsuki et al., U.S. Patent 3,338,992 and 3,341,394 to Kinney, U.S. Patent 3,502,763 to Harman, U.S. Patent 3,502,538 to Petersen, and U.S. Patent 3,542,615 to Dobo et al., each of which is incorporated herein in its entirety by reference. Spunbond fibers are quenched and generally not tacky when they are deposited onto a collecting surface. Spunbond fibers are generally continuous and often have average diameters larger than about 7 microns, more particularly, between about 10 and 30 microns.

The term "meltblown fibers" means fibers formed by extruding a molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity heated gas (e.g., air) streams which attenuate the filaments of molten thermoplastic material to reduce their diameter, which may be microfiber diameter. Thereafter, the meltblown fibers are carried by the high velocity gas stream and are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers. Such a process is disclosed for example, in U.S. Patent Number 3,849,241 to Butin et al. Meltblown fibers are microfibers which may be continuous or discontinuous, are generally smaller than 10 microns in diameter, and are generally self bonding when deposited onto a collecting surface. Meltblown fibers used in the present invention are substantially continuous in length.

The term "pulp fibers" refers to fibers from natural sources such as woody and non-woody plants. Woody plants include, for example, deciduous and coniferous trees. Non-woody plants include, for instance, cotton, flax, esparto grass, milkweed, straw, jute hemp, and bagasse.

The term "average pulp fiber length" refers to a weighted average length of pulp determined using a Kajaani fiber analyzer Model No. FS-100 available from Kajaani Oy Electronics in Kajaani, Finland. Under the test procedure, a fiber sample is treated with a macerating liquid to ensure that no fiber bundles or shives are present. Each fiber sample is dispersed in hot water and diluted to about a 0.001% concentration. Individual test samples are drawn in approximately 50 to 500 ml portions from the dilute solution and tested

using the standard Kajaani fiber analysis procedure. The weighted average fiber lengths may be expressed by the following equation:

$$\sum_{X_i > 0}^k (X_i * n_i) / n$$

where k = maximum fiber length,
 X_i = individual fiber length,
 n_i = number of fibers having length X_i ,
 and n = total number of fibers measured.

The term "superabsorbent material" refers to a water swellable, water-insoluble organic or inorganic material capable, under the most favorable conditions, of absorbing at least about 20 times its weight, preferably at least about 30 times its weight in an aqueous solution containing 0.9% by weight sodium chloride.

The term "polymer" generally includes without limitation homopolymers, copolymers (including, for example, block, graft, random and alternating copolymers), terpolymers, etc., and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible geometrical configurations of the material. These configurations include, but are not limited to isotactic, syndiotactic and atactic symmetries.

The term "bicomponent filaments or fibers" refers to fibers which have been formed from at least two polymers extruded from separate extruders but spun together to form one fiber. The polymers are arranged in substantially constantly positioned distinct zones across the cross-section of the bicomponent fibers and extend continuously along the length of the bicomponent fibers. The configuration of such a bicomponent fiber may be, for example, a sheath/core arrangement wherein one polymer is surrounded by another, or may be a side-by-side arrangement or an "islands-in-the-sea" arrangement. Bicomponent fibers are taught in U.S. Patent 5,108,820 to Kaneko et al., U.S. Patent 5,336,552 to Strack et al., and U.S. Patent 5,382,400 to Pike et al., each of which is incorporated herein in its entirety by reference. For two component fibers, the polymers may be present in ratios of 75/25, 50/50, 25/75 or any other desired ratios. Conventional additives, such as pigments and surfactants, may be incorporated into one or both polymer streams, or applied to the filament surfaces.

The term "substantially continuous filaments of fibers" refers to filaments or fibers prepared by extrusion from a spinnerette, including without limitation spunbonded and meltblown fibers, which are not cut from their original length prior to being formed into a nonwoven web or fabric. Substantially continuous filaments or fibers may have average lengths ranging from greater than about 15 cm to more than one meter, and up to the length of the nonwoven web or fabric being formed. The definition of "substantially continuous filaments or fibers" includes those which are not cut prior to being formed into a nonwoven web or fabric, but which are later cut when the nonwoven web or fabric is cut.

The term "staple fibers" means fibers which are natural or cut from a manufactured filament prior to forming into a web, and which have an average length ranging from about 0.1-15 cm, more commonly about 0.2-7 cm.

The term "personal care absorbent article" includes diapers, training pants, swim wear, absorbent underpants, baby wipes, adult incontinence products, and feminine hygiene products.

The term "through-air bonding" or "TAB" means a process of bonding a nonwoven, for example, a bicomponent fiber web in which air which is sufficiently hot to melt one of the polymers of which the fibers of the web are made is forced through the web. The air velocity is often between 100 and 500 feet per minute and the dwell time may be as long as 6 seconds. The melting and resolidification of the polymer provides the bonding. Through-air bonding has restricted variability and is generally regarded as a second step bonding process. Since TAB requires the melting of at least one component to accomplish bonding, it is restricted to webs with two components such as bicomponent fiber webs or webs containing an adhesive fiber or powder.

The term "thermal point bonding" involves passing a fabric or web of fibers to be bonded between a heated calender roll and an anvil roll. The calender roll is usually, though not always, patterned in some way so that the entire fabric is not bonded across its entire surface. As a result, various patterns for calender rolls have been developed for functional as well as aesthetic reasons. One example of a pattern has points and is the Hansen Pennings or "H&P" pattern with about a 30% bond area with about 200 bonds/square inch as taught in U.S. Patent 3,855,046 to Hansen and Pennings. The H&P pattern has square point or pin bonding areas wherein each pin has a side dimension of 0.038 inches

(0.965 mm), a spacing of 0.070 inches (1.778 mm) between pins, and a depth of bonding of 0.023 inches (0.584 mm). The resulting pattern has a bonded area of about 29.5%. Another typical point bonding pattern is the expanded Hansen and Pennings or "EHP" bond pattern which produces a 15% bond area with a square pin having a side dimension of 0.037 inches (0.94 mm), a pin spacing of 0.097 inches (2.464 mm) and a depth of 0.039 inches (0.991 mm). Another typical point bonding pattern designated "714" has square pin bonding areas wherein each pin has a side dimension of 0.023 inches, a spacing of 0.062 inches (1.575 mm) between pins, and a depth of bonding of 0.033 inches (0.838 mm). The resulting pattern has a bonded area of about 15%. Yet another common pattern is the C-Star pattern which has a bond area of about 16.9%. The C-Star pattern has a cross-directional bar or "corduroy" design interrupted by shooting stars. Other common patterns include a diamond pattern with repeating and slightly offset diamonds and a wire weave pattern looking as the name suggests, e.g., like a window screen. Typically, the percent bonding area varies from around 10% to around 30% of the area of the fabric laminate web. As is well known in the art, the spot bonding holds the laminate layers together as well as imparts integrity to each individual layer by bonding filaments and/or fibers within each layer.

DETAILED DESCRIPTION OF THE PRESENTLY PREFERRED EMBODIMENTS

The present invention is directed to an absorbent composite nonwoven web composite including substantially continuous bicomponent thermoplastic filaments and pulp fibers contained among the filaments. The absorbent nonwoven web composite contains from about 5-97% by weight pulp fibers and about 3-95% by weight substantially continuous bicomponent thermoplastic filaments. Preferably, the absorbent nonwoven web composite contains about 35-95% by weight pulp fibers and about 5-65% by weight substantially continuous bicomponent thermoplastic filaments. More preferably, the absorbent nonwoven web composite contains about 50-95% by weight pulp fibers and about 5-50% by weight substantially continuous bicomponent thermoplastic filaments.

The substantially continuous bicomponent thermoplastic filaments may have any of the bicomponent configurations described above. Preferably, the filaments have either a side-by-side configuration or a sheath-core configuration. In these configurations, both the filaments and the polymers within the filaments are substantially continuous in

length. The substantially continuous filaments may be spunbond filaments or meltblown microfibers, and typically have an average diameter of about 1-75 microns. Preferably, the substantially continuous filaments have an average diameter of about 1-50 microns, more preferably about 1-30 microns. Other processes for forming substantially continuous filaments may also be employed. The filaments may be crimped, using techniques available to persons skilled in the art.

The substantially continuous bicomponent filaments contain at least two thermoplastic polymers. Preferably, the substantially continuous bicomponent filaments contain a first polymer which imparts a first desirable property to the filaments, and a second polymer which imparts a second desirable property to the filaments. Examples of first and second desirable properties include without limitation durability and softness, durability and wettability, wettability and softness, durability and aesthetic appearance, and other desirable combinations. Of course, the first polymer may contribute one or more desirable properties, and the second polymer may contribute one or more additional desirable properties. Also, the bicomponent filaments may include more than two distinct polymers, with each polymer contributing unique properties. Furthermore, the bicomponent filaments may include a distinct polymer blend having desirable properties, adjacent to another distinct polymer or polymer blend. Additives, such as pigments and hydrophilic modifiers, may be incorporated into one or both polymers, or applied to the filament surfaces.

Examples of polymer components which contribute durability to bicomponent filament webs include without limitation polypropylene homopolymers, polypropylene copolymers containing up to about 10% ethylene or another C₄-C₂₀ alpha-olefin comonomer, high density polyethylenes, linear low density polyethylenes in which the alpha-olefin comonomer content is less than about 10% by weight, polyamides, polyesters, polycarbonates, polytetrafluoroethylenes, and other high tensile materials. Generally, a first polymer can be said to contribute durability to bicomponent filaments when a nonwoven web made from bicomponent filaments containing a first polymer and a second polymer withstands a tensile load which is at least about 10% greater, and preferably at least about 30% greater, than a similar nonwoven web made from similar filaments containing the second polymer alone.

Examples of polymer components which contribute flexibility and softness to bicomponent filament webs include without limitation high pressure (branched) low density polyethylenes, linear low density polyethylenes in which the alpha-olefin comonomer content is more than about 10% by weight, copolymers of ethylene with at least one vinyl monomer (for example, ethylene vinyl acetate), copolymers of ethylene with unsaturated aliphatic carboxylic acids (including ester derivatives thereof) and copolymers of any two alpha-olefins having 2-20 carbon atoms wherein the content of each of the two comonomers exceeds 10% by weight of the copolymer (including, for instance, ethylene-propylene rubbers). Also included are thermoplastic polyurethanes, A-B and A-B-A' block copolymers where A and A' are thermoplastic end blocks and B is an elastomeric block. Generally, a second polymer can be said to contribute flexibility and/or softness to a bicomponent nonwoven web when a nonwoven web made from filaments containing a first polymer and the second polymer is more flexible, and/or has a softer feel, than a similar nonwoven web made from similar filaments containing the first polymer alone.

Examples of polymers which contribute wettability to a thermoplastic nonwoven web include without limitation polyamides, polyvinyl acetates, saponified polyvinyl acetates, saponified ethylene vinyl acetates, and other hydrophilic materials. A second polymer generally contributes to the wettability of bicomponent filaments if a droplet of water positioned on a nonwoven web made from bicomponent filaments containing first and second polymers has a contact angle which is a) less than 90 degrees measured using ASTM D724-89, and b) less than the contact angle of a similar nonwoven web made from similar filaments containing only the first polymer. When used as an outer layer in a sheath/core bicomponent filament web, the hydrophilic polymer imparts surface wettability to the entire web.

Of course, the ability of polymers to contribute desirable properties to nonwoven bicomponent filaments requires that there be a sufficient amount of each polymer in the filaments. Generally, the substantially continuous thermoplastic filaments contain about 10-90% by weight of the first selected polymer and about 10-90% by weight of the second selected polymer. The bicomponent filaments will preferably include about 25-75% by weight of each polymer, more preferably about 40-60% by weight of each polymer.

The substantially continuous thermoplastic bicomponent nonwoven filaments may be combined with pulp fibers using processes well known in the art. For example, a coform process may be employed, in which at least one meltblown diehead is arranged near a chute through which other materials are added while the web is forming. Coform processes are described in U.S. Patent 4,818,464 to Lau and 4,100,324 to Anderson et al., the disclosures of which are incorporated by reference. The substantially continuous bicomponent filaments and pulp fibers may also be combined using hydraulic entangling or mechanical entangling. A hydraulic entangling process is described in U.S. Patent 3,485,706 to Evans, the disclosure of which is incorporated by reference.

The pulp fibers may be any high-average fiber length pulp, low-average fiber length pulp, or mixtures of the same. Preferred pulp fibers include cellulose fibers. The term "high average fiber length pulp" refers to pulp that contains a relatively small amount of short fibers and non-fiber particles. High fiber length pulps typically have an average fiber length greater than about 1.5 mm, preferably about 1.5-6 mm, as determined by an optical fiber analyzer, such as the Kajaani tester referenced above. Sources generally include non-secondary (virgin) fibers as well as secondary fiber pulp which has been screened. Examples of high average fiber length pulps include bleached and unbleached virgin softwood fiber pulps.

The term "low average fiber length pulp" refers to pulp that contains a significant amount of short fibers and non-fiber particles. Low average fiber length pulps have an average fiber length less than about 1.5 mm, preferably about 0.7-1.2 mm, as determined by an optical fiber analyzer such as the Kajaani tester referenced above. Examples of low fiber length pulps include virgin hardwood pulp, as well as secondary fiber pulp from sources such as office waste, newsprint, and paperboard scrap.

Examples of high average fiber length wood pulps include those available from the U.S. Alliance Coosa Pines Corporation under the trade designations Longlac 19, Coosa River 56, and Coosa River 57. The low average fiber length pulps may include certain virgin hardwood pulp and secondary (i.e., recycled) fiber pulp from sources including newsprint, reclaimed paperboard, and office waste. Mixtures of high average fiber length and low average fiber length pulps may contain a predominance of low average fiber length pulps. For example, mixtures may contain more than about 50% by weight low-average

fiber length pulp and less than about 50% by weight high-average fiber length pulp. One exemplary mixture contains about 75% by weight low-average fiber length pulp and about 25% by weight high-average fiber length pulp.

The pulp fibers may be unrefined or may be beaten to various degrees of refinement. Crosslinking agents and/or hydrating agents may also be added to the pulp mixture. Debonding agents may be added to reduce the degree of hydrogen bonding if a very open or loose nonwoven pulp fiber web is desired. One exemplary debonding agent is available from the Quaker Oats Chemical Company, Conshohocken, Pennsylvania, under the trade designation Quaker 2008. The addition of certain debonding agents in the amount of, for example, 1-4% by weight of the composite, may reduce the measured static and dynamic coefficients of friction and improve the abrasion resistance of the thermoplastic continuous polymer filaments. The debonding agents act as lubricants or friction reducers. Debonded pulp fibers are commercially available from Weyerhaeuser Corp. under the designation NB 405.

Various improvements and alternative embodiments are also considered to be within the scope of the invention. In one embodiment, the continuous bicomponent thermoplastic filaments are combined with other thermoplastic filaments in addition to pulp fibers. For instance, the continuous bicomponent thermoplastic filaments may include a mixture of bicomponent spunbond filaments and bicomponent meltblown filaments. In this embodiment, the spunbond filaments impart greater strength and the meltblown filaments are more effective in capturing and entangling the pulp fibers.

In still another embodiment, the continuous bicomponent filaments may be spunbond and mixed with meltblown fibers (not necessarily bicomponent) which have a relatively low melting point. The composite web may thus be formed by combining three or more streams of bicomponent spunbond filaments, lower melting meltblown filaments and pulp fibers. The meltblown filaments may still be hot and tacky when the pulp fibers are introduced, and may fuse with the pulp fibers to help consolidate the structure. Meltblown microfibers, which typically have diameters much smaller than spunbond fibers, may in effect serve as a binder or adhesive for the pulp fibers.

In another embodiment, an elastic polymer may be combined with an inelastic polymer in side-by-side bicomponent filaments to produce substantially continuous

bicomponent filaments having a tendency to crimp. The substantially continuous crimped bicomponent filaments may be in the form of meltblown microfibers, which are relatively fine and flexible, to help ensnare and entangle the pulp fibers. The crimped bicomponent filaments may also be spunbond filaments, for added loft and resilience. Crimped bicomponent filaments can be used with or without other thermoplastic filaments in a nonwoven web to provide enhanced bulk and lower web density.

Exemplary combinations of elastic and inelastic materials, useful for producing substantially continuous crimped bicomponent filaments, include without limitation the following:

Relatively Elastic Polymers	Relatively Inelastic Polymers
Styrene-butadiene copolymer	Polypropylene
Styrene-butadiene copolymer	Polyethylene
Elastomeric (single site or metallocene catalyzed) polypropylene	Polypropylene or polyethylene
Elastomeric (single site or metallocene catalyzed) polyethylene	Polyethylene or polypropylene
Polyurethane	Polypropylene or polyethylene
Ethylene vinyl acetate copolymer	Polypropylene or polyethylene
Ethylene propylene rubber	Polypropylene or polyethylene

Notes: 1. Unless otherwise indicated, polymers are not made using a metallocene catalyst.

2. Unless otherwise indicated, polypropylene polymers are substantially isotactic.

In addition to combinations of elastic and inelastic polymers, other polymers combinations can be employed to achieve crimping. For instance, crimping may be achieved using combinations of heat shrinkable polymers (polymers whose filaments shrink upon secondary heating to a temperature below the melting peak) with non-heat shrinkable polymers in the substantially continuous bicomponent thermoplastic filaments. Exemplary combinations of heat shrinkable and non-heat shrinkable polymers include without limitation the following:

Relatively Heat Shrinkable Polymers	Relatively Non-Heat Shrinkable Polymers
Polyethylene terephthalate	Polyethylene or polypropylene
Polybutylene terephthalate	Polyethylene or polypropylene
Ethylene vinyl acetate copolymer	Polyethylene or polypropylene

Certain other polymer combinations also result in shrinkage, when extended side-by-side in a substantially continuous thermoplastic bicomponent filament. These combinations include, without limitation, the following:

First Polymer	Second Polymer
Lower viscosity polymer	Higher viscosity polymer
Polypropylene	Polyethylene
Polypropylene	Atactic polypropylene
Polyethylene	Atactic polypropylene

In another highly advantageous embodiment, a quantity of a superabsorbent material is combined with the substantially continuous bicomponent thermoplastic polymer filaments and pulp fibers, to improve the absorbency of the absorbent nonwoven web composite. The term "superabsorbent" or "superabsorbent material" refers to a water-swellaable, water-insoluble organic or inorganic material capable, under the most favorable conditions, of absorbing at least about 20 times its weight and, more desirably, at least about 30 times its weight in an aqueous solution containing 0.9 weight percent sodium chloride.

The superabsorbent materials can be natural, synthetic and modified natural polymers and materials. In addition, the superabsorbent materials can be inorganic materials, such as silica gels, or organic compounds such as cross-linked polymers. The term "cross-linked" refers to any means for effectively rendering normally water-soluble materials substantially water insoluble but swellaable. Such means can include, for example, physical entanglement, crystalline domains, covalent bonds, ionic complexes and associations, hydrophilic associations, such as hydrogen bonding, and hydrophobic associations or Van der Waals forces.

Examples of synthetic superabsorbent material polymers include the alkali metal and ammonium salts of poly(acrylic acid) and poly(methacrylic acid), poly(acrylamides), poly(vinyl ethers), maleic anhydride copolymers with vinyl ethers and alpha-olefins, poly(vinyl pyrrolidone), poly(vinylmorpholinone), poly(vinyl alcohol), and mixtures and copolymers thereof. Further superabsorbent materials include natural and modified natural polymers, such as hydrolyzed acrylonitrile-grafted starch, acrylic acid grafted starch, methyl cellulose, chitosan, carboxymethyl cellulose, hydroxypropyl cellulose,

and the natural gums, such as alginates, xanthan gum, locust bean gum and the like. Mixtures of natural and wholly or partially synthetic superabsorbent polymers can also be useful in the present invention. Other suitable absorbent gelling materials are disclosed by Assarsson et al. in U.S. Patent 3,901,236 issued August 26, 1975. Processes for preparing synthetic absorbent gelling polymers are disclosed in U.S. Patent No. 4,076,633 issued February 28, 1978 to Masuda et al. and U.S. Patent No. 4,286,082 issued August 25, 1981 to Tsubakimoto et al.

Superabsorbent materials may be xerogels which form hydrogels when wetted. The term "hydrogel," however, has commonly been used to also refer to both the wetted and unwetted forms of the superabsorbent polymer material. The superabsorbent materials can be in many forms such as flakes, powders, particulates, fibers, continuous fibers, networks, solution spun filaments and webs. The particles can be of any desired shape, for example, spiral or semi-spiral, cubic, rod-like, polyhedral, etc. Needles, flakes, fibers, and combinations may also be used.

When used, the superabsorbent material may be present within the absorbent nonwoven composite in an amount from about 5 to about 90 weight percent based on total weight of the absorbent nonwoven composite. Preferably, the superabsorbent constitutes about 10-60% by weight of the absorbent nonwoven web composite, more preferably about 20-50% by weight. Superabsorbents are generally available in particle sizes ranging from about 20 to about 1000 microns. Examples of commercially available particulate superabsorbents include SANWET® IM 3900 and SANWET® IM-5000P, available from Hoescht Celanese located in Portsmouth, Virginia, DRYTECH® 2035LD available from Dow Chemical Co. located in Midland, Michigan, and FAVOR® 880, available from Stockhausen, located in Greensborough, N.C. An example of a fibrous superabsorbent is OASIS® 101, available from Technical Absorbents, located in Grimsby, United Kingdom.

The superabsorbents may be added using the same techniques described above for combining the pulp fibers and continuous bicomponent nonwoven filaments. For instance, the superabsorbent can be added with the pulp into the forming stream for the bicomponent filaments as they are being extruded onto a conveyor to form a nonwoven web, or at a later point in the forming stream, separate from the pulp. Alternatively, the superabsorbent can be added to a nonwoven web using a hydraulic entangling process.

After combining the ingredients, the absorbent nonwoven composite may be binded together using the through-air bonding techniques described above, to provide a coherent high integrity structure.

The absorbent nonwoven composite of the invention can be used in a wide variety of absorbent products including, in particular, personal care absorbent articles. Personal care absorbent articles include diapers, training pants, swim wear, absorbent underpants, baby wipes, adult incontinence products, feminine hygiene products, and the like. The absorbent nonwoven composite is particularly useful in diapers, wherein the substantially continuous bicomponent filaments contribute liquid distribution, softness and durability, while the pulp and (optional) superabsorbent contribute a high level of absorbency. In one useful embodiment of the absorbent nonwoven composite, the substantially continuous bicomponent filaments are made from a side-by-side or sheath/core combination of low density or linear low density polyethylene (which contributes softness) and polypropylene (which contributes durability). If a sheath/core configuration is employed, the polypropylene should be in the core, and surrounded by a sheath of low density or linear low density polyethylene. The absorbent nonwoven composite can also be used in absorbent medical products, including without limitation underpads, bandages, absorbent drapes, and medical wipes which contain alcohol and/or other disinfectants.

Examples

Absorbent nonwoven web composites were prepared using a combination of crimped bicomponent spunbond filaments, pulp, and superabsorbent. The crimped bicomponent filaments had a side-by-side configuration and average denier of 1.5. The crimped bicomponent filaments were formed using the process described in U.S. Patent 5,382,400, issued to Pike et al. The two sides had the following compositions, with percentages based on the weight of the entire filaments.

Side A	Side B
48.0% Exxon 3445 polypropylene	49.0% Dow 61800 linear low density
1% TiO ₂	polyethylene
1% Masil SF-19 internal surfactant	1.0% Union Carbide DS4DOS copolymer

The filaments were exposed to a charge of 24.5 KV (0.0005 Amps) immediately after extrusion and quenching, to increase their efficiency in capturing the pulp

and superabsorbent material. The charge was applied using an array of three charge bars and a ground bar, positioned on opposite sides of the filaments. Then, a combination of pulp fibers and superabsorbent material was injected into the filament stream using air assist, before the bicomponent filaments were deposited onto a web forming conveyor. After depositing on the conveyor, the nonwoven web composite was subjected to through-air bonding at 264 °F, to cause improved bonding between the ingredients.

For all composite samples, the pulp used was CR1654 from Coosa Pines Co. The superabsorbent was FAVOR® 880 from Stockhausen. The prepared samples were evaluated for saturated capacity and tensile testing using the following procedures.

Saturated Capacity

A 6" X 9" sample of composite material was soaked for 20 minutes in saline (0.9% solution). Then, the sample was desorbed on a vacuum box at 0.5 psi for 5 minutes. The capacity of each sample was calculated as the weight of the wet sample minus the weight of the dry sample, the difference being divided by the dry sample weight.

Tensile Testing

The tensile tests were performed according to the INDA Strip Tensile test procedure IST 110.1-92. Each sample was 3" wide instead of the 2" width described in the IST 110.1-92 procedure. The parameters of the tensile test are described below:

- Cross head speed: 12" per minute
- Load cell: 100 N
- Gage Length: 3"
- Constant rate of extension

The wet tests (below) were carried out on samples which had been saturated according to the saturated capacity test procedure described above. These samples were in saline for 20 minutes and excess liquid was desorbed with 0.5 psi of vacuum for 5 minutes.

Table 1 sets forth the compositions of the samples prepared. Example 1 reflects a control sample containing only pulp and superabsorbent, and no bicomponent filament matrix. Examples 2 and 4 reflect the use of a bicomponent filament matrix with pulp fibers, but without superabsorbent. The amount of pulp was twice as large for Example 2, as for Example 4. Examples 3 and 5 reflect the use of a bicomponent filament matrix with

pulp fibers and superabsorbent. Example 5 utilized less pulp fibers and more superabsorbent than Example 3.

Table 1: Description of Samples

Example No.	Composite Overall Basis wt. (gsm)	Bico Fiber Basis wt. (gsm)	% Bico fiber	Pulp Basis wt. (gsm)	% Pulp	Super Absorbent Basis wt. (gsm)	% Super Absorbent	Bico Fibers Charged
1	550	0.0	0%	220	40%	330	60%	NA
2	150	85	57%	65	43%	0.0	0%	Yes
3	265	85	32%	100	38%	80	30%	No
4	108	85	79%	23	21%	0.0	0%	No
5	198	85	43%	23	12%	90	45%	Yes

Table 2 sets forth the test results for each Example. All of the tensile properties showed dramatically better results for the inventive samples, compared to the control. The inventive samples also retained considerable saturated capacity, most notably where superabsorbent material was used.

Table 2: Evaluation Of Examples

Example No.	Saturated Capacity (g/g)	Dry Tensile Load (g)	Dry Load/Basis wt. (g/gsm)	Dry % Strain	Wet Tensile Load (g)	Wet Load/Basis wt. (g/gsm)	Wet % Strain
1	20.5	154	0.28	7%	0	0.0	0%
2	10.4	2157	14.38	25%	2665	17.77	27%
3	15.4	1986	7.49	22%	1706	6.44	32%
4	11.7	3059	28.32	23%	2793	25.86	25%
5	15.9	1989	10.05	24%	2458	12.41	28%

While the embodiments of the invention described herein are presently considered preferred, various modifications and improvements can be made without departing from the spirit and scope of the invention. The scope of the invention is indicated by the appended claims, and all changes within the meaning and range of equivalents are intended to be embraced therein.

WE CLAIM:

1. An absorbent nonwoven web composite, comprising:
a plurality of substantially continuous bicomponent filaments including a first thermoplastic polymer and a second thermoplastic polymer arranged in distinct zones across a cross-section of individual bicomponent filaments; and
a plurality of pulp fibers contained within the substantially continuous filaments.
2. The absorbent nonwoven web composite of Claim 1, wherein the first and second thermoplastic polymers are arranged in a side-by-side configuration.
3. The absorbent nonwoven web composite of Claim 1, wherein the first and second thermoplastic polymers are arranged in a sheath/core configuration.
4. The absorbent nonwoven web composite of Claim 1, wherein the first polymer comprises a relatively durable polymer selected from the group consisting of polypropylene homopolymers and copolymers containing up to about 10% by weight of an alpha-olefin comonomer, high density polyethylene, linear low density polyethylene having an alpha-olefin comonomer content less than about 10% by weight, polyamides, polyesters, polycarbonates, polytetrafluoroethylenes, and combinations thereof.
5. The absorbent nonwoven web composite of Claim 1, wherein the second polymer comprises a relatively soft polymer selected from the group consisting of branched low density polyethylene, linear low density polyethylene having an alpha-olefin comonomer content of more than about 10% by weight, copolymers of ethylene with at least one vinyl comonomer, copolymers of ethylene with unsaturated aliphatic carboxylic acids and ester derivatives thereof, other copolymers of any two alpha-olefins having up to 20 carbon atoms wherein the content of each of the two comonomers exceeds about 10% by weight of the copolymer, and combinations thereof.

6. The absorbent nonwoven web composite of Claim 1, wherein the second polymer comprises a wettable polymer different from the first polymer and selected from the group consisting of polyamides, polyvinyl acetates, saponified polyvinyl acetates, saponified ethylene vinyl acetates, other hydrophilic polymers, and combinations thereof.

7. The absorbent nonwoven web composite of Claim 1, wherein the first thermoplastic polymer contributes durability and the second thermoplastic polymer contributes softness.

8. The absorbent nonwoven web composite of Claim 1, wherein the first thermoplastic polymer contributes wettability and the second thermoplastic polymer contributes softness.

9. The absorbent nonwoven web composite of Claim 1, wherein the first thermoplastic polymer contributes durability and the second thermoplastic polymer contributes wettability.

10. The absorbent nonwoven web composite of Claim 1, wherein the substantially continuous bicomponent filaments comprise crimped filaments.

11. The absorbent nonwoven web composite of Claim 10, wherein the first thermoplastic polymer comprises a relatively elastic polymer and the second thermoplastic polymer comprises a relatively inelastic polymer.

12. The absorbent nonwoven web composite of Claim 10, wherein the first thermoplastic polymer comprises a relatively heat shrinkable polymer and the second thermoplastic polymer comprises a relatively non-heat shrinkable polymer.

13. The absorbent nonwoven web composite of Claim 1, wherein the pulp comprises low average fiber length pulp having an average fiber length less than about 1.5 mm.

14. The absorbent nonwoven web composite of Claim 1, wherein the pulp comprises high average fiber length pulp having an average fiber length of about 1.5-6 mm.

15. The absorbent nonwoven web composite of Claim 1, wherein the pulp comprises a mixture of low average fiber length pulp and high average fiber length pulp.

16. The absorbent nonwoven web composite of Claim 1, comprising about 5-97% by weight of the pulp fibers and about 3-95% by weight of the substantially continuous bicomponent filaments.

17. The absorbent nonwoven web composite of Claim 1, comprising about 35-95% by weight of the pulp fibers and about 5-65% by weight of the substantially continuous bicomponent filaments.

18. The absorbent nonwoven web composite of Claim 1, comprising about 50-95% by weight of the pulp fibers and about 5-50% by weight of the substantially continuous bicomponent filaments.

19. The absorbent nonwoven web composite of Claim 1, further comprising about 5-90% by weight of a superabsorbent material.

20. The absorbent nonwoven web composite of Claim 19, comprising about 10-60% by weight of the superabsorbent material.

21. The absorbent nonwoven web composite of Claim 19, comprising about 20-50% by weight of the superabsorbent material.

22. An absorbent nonwoven web composite, comprising:

a plurality of substantially continuous bicomponent filaments comprising a propylene polymer and an ethylene polymer arranged in distinct zones across a cross-section of individual bicomponent filaments; and

a plurality of pulp fibers contained within the substantially continuous filaments.

23. The absorbent nonwoven web composite of Claim 22, wherein the pulp fibers comprise cellulose fibers.

24. The absorbent nonwoven web composite of Claim 22, wherein the propylene polymer comprises a polypropylene homopolymer or copolymer containing up to about 10% by weight ethylene.

25. The absorbent nonwoven web composite of Claim 22, wherein the ethylene polymer comprises low density polyethylene.

26. The absorbent nonwoven web composite of Claim 22, further comprising a superabsorbent.

27. A personal care absorbent article, comprising:

an absorbent nonwoven web including about 5-90% by weight pulp fibers, 0-90% by weight of a superabsorbent, and about 3-95% by weight substantially continuous bicomponent filaments including a first thermoplastic polymer "A" and a second thermoplastic polymer "B,"

the first thermoplastic polymer "A" imparting a first desirable property to the nonwoven web,

the second thermoplastic polymer "B" imparting a second desirable property to the nonwoven web.

28. The absorbent article of Claim 27, comprising a diaper.
29. The absorbent article of Claim 27, comprising training pants.
30. The absorbent article of Claim 27, comprising absorbent underpants.
31. The absorbent article of Claim 27, comprising an adult incontinence article.
32. The absorbent article of Claim 27, comprising a feminine hygiene article.
33. The absorbent article of Claim 27, comprising swim wear.
34. The absorbent article of Claim 27, comprising a baby wipe.
35. The absorbent article of Claim 27, wherein the first thermoplastic polymer "A" and second thermoplastic polymer "B" are arranged in a side-by-side configuration.
36. The absorbent article of Claim 27, wherein the first thermoplastic polymer "A" and second thermoplastic polymer "B" are arranged in a sheath/core configuration.
37. The absorbent article of Claim 27, wherein the first thermoplastic polymer "A" comprises a propylene polymer and the second thermoplastic polymer "B" comprises an ethylene polymer.

38. The absorbent article of Claim 27, wherein the propylene polymer comprises a propylene homopolymer or copolymer containing up to about 10% by weight ethylene.

39. The absorbent article of Claim 27, wherein the ethylene polymer comprises low density polyethylene.

40. The absorbent article of Claim 27, wherein the first desirable property comprises durability, and the second desirable property comprises softness.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/26526

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 D04H5/02 D01F8/06 D01F8/12 D01F8/14 D04H1/42
D04H3/10 D04H1/46 D21H15/06 D21H15/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D04H D01F A61F D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 45519 A (FIBERVISIONS A S) 15 October 1998 (1998-10-15) page 5, line 7 - line 32 page 7, line 6 - line 20; claims; examples	1-40
A	EP 0 216 520 A (TORAY INDUSTRIES) 1 April 1987 (1987-04-01) page 5, line 14 - line 30	1-40
A	US 5 759 926 A (PIKE RICHARD DANIEL ET AL) 2 June 1998 (1998-06-02) the whole document	1-40
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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G document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Internat. Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p> DATABASE WPI Section Ch, Week 199545 Derwent Publications Ltd., London, GB; Class A96, AN 1995-347491 XP002135473 & JP 07 236653 A (MITSUI PETROCHEM IND CO LTD), 12 September 1995 (1995-09-12) abstract </p>	1-40
A	<p> EP 0 340 763 A (DANAKLON AS) 8 November 1989 (1989-11-08) the whole document </p>	1-40

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internati Application No

PCT/US 99/26526

Patent document cited in search report		Publication dat	Patent family member(s)	Publication date
WO 9845519	A	15-10-1998	AU 6918298 A EP 0973966 A US 5981410 A	30-10-1998 26-01-2000 09-11-1999
EP 0216520	A	01-04-1987	JP 1912321 C JP 6039740 B JP 62045764 A JP 1015614 B JP 1531886 C JP 62078247 A DE 3686928 A US 4774110 A US 4735849 A	09-03-1995 25-05-1994 27-02-1987 17-03-1989 24-11-1989 10-04-1987 12-11-1992 27-09-1988 05-04-1988
US 5759926	A	02-06-1998	AU 707668 B AU 5939196 A CA 2221135 A EP 0830466 A WO 9641041 A	15-07-1999 30-12-1996 19-12-1996 25-03-1998 19-12-1996
JP 7236653	A	12-09-1995	NONE	
EP 0340763	A	08-11-1989	AT 112593 T AU 626554 B AU 3732289 A CA 1334047 A CN 1037555 A CS 8902767 A DE 68918627 D DE 68918627 T DK 263790 A WO 8910989 A ES 2012024 T JP 3504144 T KR 9615656 B MX 15943 A NO 177192 B NZ 228981 A PT 90447 A RU 2079585 C US 5456982 A	15-10-1994 06-08-1992 29-11-1989 24-01-1995 29-11-1989 15-01-1991 10-11-1994 16-02-1995 03-01-1991 16-11-1989 01-12-1994 12-09-1991 20-11-1996 28-02-1994 24-04-1995 25-06-1991 30-11-1989 20-05-1997 10-10-1995